Short communication

Insertion-induced expansion of a thin film on a rigid substrate

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HIGHLIGHTS

- A mathematic treatment of insertion-induced expansion of a thin film was developed.
- A semi-analytical relation is obtained for insertion-induced expansion of a Si film.
- Stress-assisted diffusion is important in controlling diffusion of Li atoms in LIB.

ABSTRACT

The local volume expansion due to the insertion of lithium into electric anode in a lithium-ion battery determines the structural durability and reliability of the battery. The coupling between diffusion and stress was incorporated in analyzing the insertion-induced expansion of an elastic thin film on a rigid substrate. The results showed that the stress-assisted diffusion is an important mechanism controlling the diffusion of lithium cations in silicon films. Under the action of a constant diffusion flux, semi-analytical relations were obtained for the temporal evolution of the insertion-induced expansion of a Si film and the hydrostatic stress in the Si film. The surface displacement of the Si film is proportional to the film thickness and the square of the electric current density for small diffusion time.

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1. Introduction

Lithium-ion batteries (LIBs), which generally require a long service life under sustained electrochemical cycling, have been gradually used in hybrid electric vehicles and advanced aircraft. To develop LIBs of high energy density and high capacity, new electrode materials, such as Si and Sn, have been investigated. Many of these materials experience rapid volume changes during the insertion and de-insertion of lithium, which can reach to ∼400% in silicon, and introduce significant stresses due to geometrical confinement. The development of large stresses has limited the use of bulk structural materials of high energy density and capacity in LIBs, and has accelerated the research to develop low-dimensional materials, such as thin films, nanowires, and nanoparticles for LIBs.

Beaulieu et al. [1] used in-situ AFM to characterize the effect of the insertion and de-insertion of lithium on the volume changes of continuous and patterned films of crystalline Al, crystalline Sn, amorphous Si (a-Si), and a-Si$_{0.64}$Sn$_{0.36}$ through the measurement of

the change in length, width, and height. Tian et al. [2] measured the volume change of nanostructured Sn–Co–C films as a function of Li content. They observed the height change of the Sn–Co–C films during lithation and delithation, and the separation of the films from substrate in the central portion of the films. Park et al. [3] used in-situ AFM to investigate the time-dependent morphology change of cylindrical LixCoO2-electrodes during charging and discharging and used finite element method to analyze the morphological change of a cylindrical pillar. Maranchi et al. [4] observed the cracking and debonding of amorphous Si on the Cu-foil substrate, which was created by the insertion and de-insertion of lithium into silicon during electrochemical charging. Uia et al. [5] observed the cracking of Sn film after the first discharge when studying the electrochemical characteristics of Sn film as a negative electrode for lithium secondary batteries. Li et al. [6] examined the crack pattern on amorphous Si films in thin film lithium-ion battery electrodes. He et al. [7] used AFM to examine the shape evolution of patterned amorphous and polycrystalline Si microarray caused by Li insertion and de-insertion. They observed the change of square columns to the dome and bowl shape, and the presence of surface cracking and delamination. Yang [8] derived simple relations between the critical concentration of solute atoms and average damage size for the

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insertion-induced cracking and buckling in an elastic film. Haftbaradaran and Gao [9] used analytical and numerical calculations to reveal the occurrence of ratcheting in patterned Si islands during lithiation/delithiation cycling. Obviously, the volume change during the lithium insertion and de-insertion presents a challenge to the development of advanced LIBs for use in hybrid electric vehicles and advanced aircraft.

Understanding the volume change of active materials during lithiation/delithiation cycling plays an important role in the structural design and material selection of the next-generation LIBs, and in the prevention of the microcracking and debonding of thin films. It is the purpose of this work to study the insertion-induced expansion of an elastic thin film on a rigid substrate. The effect of the insertion-induced stress is incorporated in the analysis. The temporal evolution of the film thickness is obtained as a function of Li concentration. The variation of the hydrostatic stress in the film is also discussed.

2. Physical model

Consider an elastic film deposited on a rigid substrate. Here, the analysis is focused on the effect of the insertion of solute atoms into the film on the change of the film thickness and the evolution of hydrostatic stress. The insertion of solute atoms into the film introduces local volumetric expansion and mechanical stress, which causes the change of the film thickness and possibly local separation from the substrate.

Assume that (1) the deformation is elastic and isotropic, and the analysis is not focused on the large deformation related to plasticity [10], (2) the diffusion coefficient and mechanical properties are constants, independent of the concentration of solute atoms, and (3) the film thickness is much smaller than the lateral dimensions. The constitutive relation describing the diffusion-induced deformation of elastic materials in the regime of linear elasticity is [11]

$$\varepsilon_{ij} = \frac{1}{E}\left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}\right] + \frac{c\Omega}{3}\delta_{ij} \tag{1}$$

where ε_{ij} ($i,j = 1,2,3$) are the components of strain tensor, σ_{ij} are the components of stress tensor, Ω is the coefficient of the volume expansion per mole of solute atoms (m³ mol⁻¹), c is the concentration (mol m⁻³) of the diffusing component, and E and ν are Young's modulus and Poisson's ratio of the material, respectively. The coefficient of the volume expansion Ω is assumed constant, independent of c. Note that the material properties of E, D, and Ω can be concentration-dependent. The effect of the concentration dependence of E, D, and Ω on diffusion and chemical stress is generally negligible for a small concentration of solute atoms, and E, D, and Ω can be approximated constants, as used in this work. However, the effect of the concentration dependence of E, D, and Ω may become important in controlling atomic migration when new phases are formed and the material becomes composite.

For the film being firmly adherent to the substrate, the material experiences no lateral displacement on the contact surface. With the insertion of solute atoms into the film, the confinement of the rigid substrate introduces local mechanical strain in the film as

$$\varepsilon_{11} = \varepsilon_{22} = -\frac{c\Omega}{3} \tag{2}$$

According to symmetrical characteristics of the problem, $\sigma_{11} = \sigma_{22}$. Without the normal loading applied to the upper surface of the film, one has $\sigma_{33} = 0$. Eqs. (1) and (2) give

$$\sigma_{11} = \sigma_{22} = -\frac{E}{1-\nu}\frac{c\Omega}{3} \tag{3}$$

$$\varepsilon_{33} = \frac{2\nu}{1-\nu}\frac{c\Omega}{3} \tag{4}$$

From Eq. (3) and $\sigma_{33} = 0$, the hydrostatic stress in the film is found as

$$\sigma = \frac{\sigma_{11}+\sigma_{22}+\sigma_{33}}{3} = -\frac{2E}{1-\nu}\frac{c\Omega}{9} \tag{5}$$

Integration of Eq. (4) gives the displacement of the upper surface of the film (i.e. the thickness change of the film) as

$$u_3 = \int_0^h \varepsilon_{33}\,\mathrm{d}x_3 = \frac{2\nu}{1-\nu}\frac{\Omega}{3}\int_0^h c\,\mathrm{d}x_3 \tag{6}$$

Here, h is the film thickness.

Considering the stress effect on diffusion, one can express the diffusion equation as [11]

$$D_0\left[\nabla^2 c - \frac{\Omega}{RT}\vec{\nabla} c\cdot\vec{\nabla}\,\sigma - \frac{\Omega c}{RT}\nabla^2\sigma\right] = \frac{\partial c}{\partial t} \tag{7}$$

where D_0 is the diffusion coefficient, R is the gas constant, T is absolute temperature, and t is time. Substituting Eq. (5) into Eq. (7) gives

$$D_0\left[(1+\alpha c)\nabla^2 c + \alpha\vec{\nabla}\,c\cdot\vec{\nabla}\,c\right] = \frac{\partial c}{\partial t} \tag{8}$$

with

$$\alpha = \frac{2E\Omega^2}{9(1-\nu)RT} \tag{9}$$

For one-dimensional problems, Eq. (8) reduces to

$$D_0\left[(1+\alpha c)\frac{\partial^2 c}{\partial x_3^2} + \alpha\left(\frac{\partial c}{\partial x_3}\right)^2\right] = \frac{\partial c}{\partial t} \tag{10}$$

or

$$D_0\frac{\partial}{\partial x_3}\left[(1+\alpha c)\frac{\partial c}{\partial x_3}\right] = \frac{\partial c}{\partial t} \tag{11}$$

Eq. (11) suggests that the stress effect on the diffusion of solute atoms is equivalent to the nonlinear diffusion with the concentration dependence of the diffusion coefficient. Eq. (11) reduces to the classical diffusion equation if there is no stress effect on the diffusion of solute atoms. To completely describe the problem, one needs boundary conditions to obtain the diffusion field from Eq. (11).

3. Evolution of hydrostatic stress and film thickness

Consider the evolution of the hydrostatic stress and film thickness in the thin film. Initially, there are no solute atoms in the film, i.e. the initial condition is

$$c = 0 \quad \text{for } 0 \leq x_3 \leq h \text{ at } t = 0 \tag{12}$$

The conducting film is connected to a current collector at the end of $x_3 = 0$ and solute atoms cannot diffuse into the current collector. Thus, the boundary condition at $x_3 = 0$ is

$$\frac{\partial c}{\partial x_3} = 0 \quad \text{for } t \geq 0 \text{ at } x_3 = 0 \tag{13}$$

The polarization of an electrode supporting the electrochemical reaction, involving lithiation/delithiation cycling, at the electrolyte−electrode interface is generally represented by the Butler−Volmer relationship [12,13]. Assume that there exists a constant diffusion flux at the electrolyte−electrode interface with the characteristics of constant cycling. One has

$$\frac{\partial c}{\partial x_3} = \frac{I}{FD_0} \quad \text{for } t \geq 0 \text{ at } x_3 = h \tag{14}$$

Here, I is the current density at the electrolyte−electrode interface, which is related to the surface overpotential and the exchange-current density. F is Faraday's constant.

To determine the distribution of the concentration and the evolution of the hydrostatic stress and film thickness, we introduce the following dimensionless parameters, $\tilde{x} = x_3/h$, $\tilde{t} = D_0\tilde{\alpha}t/h^2$, $\tilde{c} = c/(Ih/FD_0)$ and $\tilde{\alpha} = \alpha Ih/FD_0$. Using finite difference approach, Eq. (10) can be approximated by the following finite difference equation,

$$\left(\tilde{\alpha}^{-1} + \tilde{c}_n^{\tilde{t}_m}\right)\frac{\tilde{c}_{n+1}^{\tilde{t}_m} - 2\tilde{c}_n^{\tilde{t}_m} + \tilde{c}_{n-1}^{\tilde{t}_m}}{(\Delta\tilde{x})^2} + \left(\frac{\tilde{c}_{n+1}^{\tilde{t}_m} - \tilde{c}_{n-1}^{\tilde{t}_m}}{2\Delta\tilde{x}}\right)^2$$
$$= \frac{\tilde{c}_n^{\tilde{t}_m+\Delta\tilde{t}} - \tilde{c}_n^{\tilde{t}_m}}{\Delta\tilde{t}} \tag{15}$$

where $\tilde{c}_n^{t_m}$ corresponds to the concentration at the position $\tilde{x} = \tilde{x}_n$ and time $\tilde{t} = \tilde{t}_m$, $\Delta\tilde{x} = \tilde{x}_{n+1} - \tilde{x}_n$ and $\Delta\tilde{t} = \tilde{t}_{m+1} - \tilde{t}_m$. The distribution of the concentration in the thin film as a function of time can then be obtained as

$$\tilde{c}_n^{\tilde{t}_m+\Delta\tilde{t}} = \tilde{c}_n^{\tilde{t}_m} + \Delta\tilde{t}\left[\left(\tilde{\alpha}^{-1} + \tilde{c}_n^{\tilde{t}_m}\right)\frac{\tilde{c}_{n+1}^{\tilde{t}_m} - 2\tilde{c}_n^{\tilde{t}_m} + \tilde{c}_{n-1}^{\tilde{t}_m}}{(\Delta\tilde{x})^2} \right.$$
$$\left. + \left(\frac{\tilde{c}_{n+1}^{\tilde{t}_m} - \tilde{c}_{n-1}^{\tilde{t}_m}}{2\Delta\tilde{x}}\right)^2\right] \tag{16}$$

In the simulation, $\Delta\tilde{x} = 0.01$, $1 \leq n \leq 101$ and $m \geq 0$. For the case where there is no stress-assisted diffusion, one needs to define the dimensionless time as $\tilde{t} = D_0t/h^2$. Eq. (16) reduces to

$$\tilde{c}_n^{\tilde{t}_m+\Delta\tilde{t}} = \tilde{c}_n^{\tilde{t}_m} + \Delta\tilde{t}\cdot\frac{\tilde{c}_{n+1}^{\tilde{t}_m} - 2\tilde{c}_n^{\tilde{t}_m} + \tilde{c}_{n-1}^{\tilde{t}_m}}{(\Delta\tilde{x})^2} \tag{17}$$

There is no coupling between diffusion and stress in controlling atomic migration.

Consider the stress evolution as introduced by the insertion of Li cations into a silicon film of 1 μm in thickness in a Li-ion battery during a charging process. The parameters are $E = 159$ GPa [14,15], $v = 0.22$ [14], $R = 8.31$ J mol^{-1} K^{-1}, $T = 298$ K, $\Omega = 7.69 \times 10^{-6}$ m^3 mol^{-1} [16], $F = 9.65 \times 10^4$ C mol^{-1}, and $D_0 = 10^{-17}$ m^2·s^{-1} [17]. The parameter α/FD_0 is calculated to be 1.12×10^9 m A^{-1}. This result suggests that one needs to consider the interaction between stress and diffusion when analyzing the stress state and the volume change in the Si film.

Fig. 1 shows the temporal variation of the Li concentration at several positions in the Si film for $I = 10^{-6}$ A cm^{-2}. The highest Li concentration always occurs at the electrolyte−electrode interface, and the smallest Li concentration is at the current collector ($\tilde{x} = 0$). Due to the diffusion characteristics, it takes time for Li cations to diffuse to the interface between the current collector and the Si film. A large difference in the Li concentration is observed at the
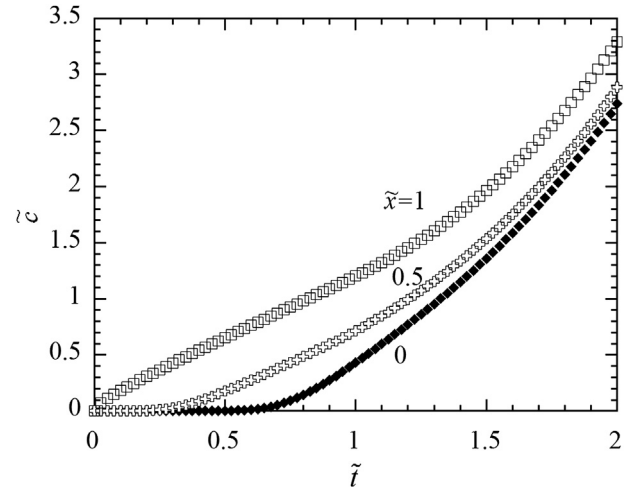

Fig. 1. Temporal variation of the Li concentration at several positions in the Si film ($I = 10^{-6}$ A cm^{-2}).

onset of the diffusion. With the increase in time, the concentration difference in the Si film decreases.

The profiles of the Li concentration in the Si film at different times are plotted in Fig. 2 for $\tilde{t} = 0.5$, 0.75, 1, 1.25, and 1.5 with $I = 10^{-6}$ A cm^{-2}. It is interesting to note that, for small values of $\tilde{t}$, linear distribution of the Li cations can be observed near the electrolyte−electrode interface. For small values of $\tilde{t}$, the migration of Li cations is controlled by the concentration gradient, and the stress-assisted diffusion is negligible. At the electrolyte−electrode interface, the concentration gradient must satisfy Eq. (14), which gives the linear distribution of Li cations. With the increase in the diffusion time, the portion of the linear distribution of the Li cations decreases. More Li cations accumulate in the Si film, which leads to the stress increase in the Si film. For large magnitude of the parameter $\tilde{\alpha}$, the diffusion of Li cations in the Si film cannot be simply described by Fick's second law. One needs to incorporate the coupling between stress and diffusion when analyzing the diffusion problems for large volume expansion of Ω or large current density.

From the concentration distribution, one can use Eq. (6) to determine the displacement of the upper surface of the Si film, which represents the insertion-induced expansion of the Si film. Fig. 3 shows the time dependence of the displacement of the upper
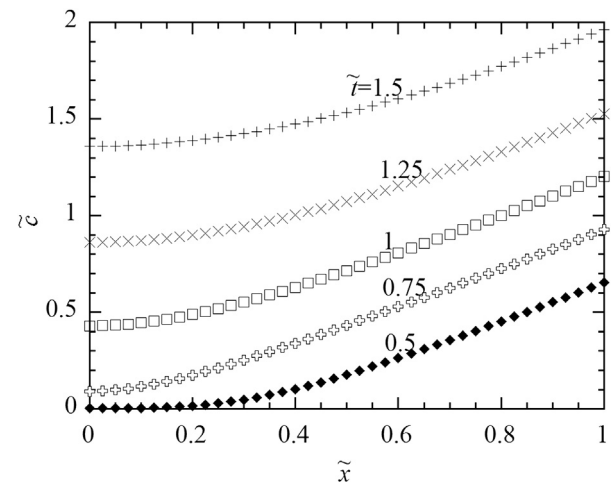

Fig. 2. Distribution of the Li concentration in the Si film at several times ($I = 10^{-6}$ A cm^{-2}).
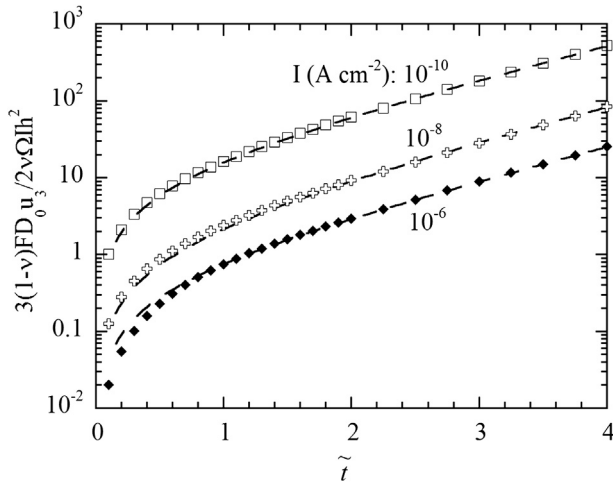
Fig. 3. Time dependence of the displacement of the upper surface of the Si film during the Li insertion.

surface of the Si film due to the insertion of Li cations for $I = 10^{-6}$, 10^{-8}, and 10^{-10} A cm^{-2} with $h = 1$ μm. The surface displacement increases with the continuous diffusion of Li cations into the Si film due to the diffusion-induced volume change. Using the best curve-fitting, one finds that the surface displacement can be approximated as

$$u_3 = \frac{2\chi(\tilde{\alpha})\nu\Omega Ih^2}{3(1-\nu)FD_0}\left(e^{\tilde{t}} - 1\right) \tag{18}$$

with $\chi(\tilde{\alpha})$ being a constant, dependent on the dimensionless parameter of $\tilde{\alpha}$. Under the condition of constant diffusion flux for the insertion of Li cations, the surface displacement of the Si film is an exponential function of time. For $\tilde{t} \ll 1$, Eq. (18) gives

$$u_3 = \frac{4\chi(\tilde{\alpha})\nu\Omega^3 EI^2 ht}{27(1-\nu)^2 RTF^2 D_0} \tag{19}$$

The surface displacement is proportional to the film thickness and the square of the electric current density.

From Eqs. (5) and (6), the average hydrostatic stress, $\langle\sigma\rangle$, and average biaxial stresses, $\langle\sigma_{11}\rangle$ and $\langle\sigma_{22}\rangle$, can be found as

$$\langle\sigma\rangle = \frac{2\langle\sigma_{11}\rangle}{3} = \frac{2\langle\sigma_{22}\rangle}{3} = -\frac{2E}{1-\nu}\frac{\Omega}{9h}\int_0^h c\,dx_3$$

$$= -\frac{2\chi(\tilde{\alpha})\Omega EIh}{9(1-\nu)FD_0}\left(e^{\tilde{t}} - 1\right) \tag{20}$$

The average hydrostatic stress is a nonlinear function of the electric current density and the film thickness.

4. Conclusion

The interaction between diffusion and stress plays an important role in controlling the structural integrity in LIBs. The migration/diffusion of Li cations in silicon cannot be simply described by the classical Fick's second law; the stress-assisted diffusion needs to be taken into account when analyzing the structural response and degradation due to the insertion/diffusion of Li cations.

The work presented here has attempted to bring out the potential importance of the insertion-induced deformation in examining the structural response resulting from electrochemical charging and discharging. In particular, the study has shown that the insertion-induced stress plays a role in controlling the mechanical deformation of Si films due to the insertion of Li cations. Semi-analytical relation is obtained for the insertion-induced expansion of a Si film as a function of time. For $\tilde{t} \ll 1$, the surface displacement is proportional to the film thickness and the square of the electric current density. Such a simple relationship provides a potential approach to determine the coefficient of the volume expansion and can be applied not only to the structural response of thin films due to the lithium insertion in LIBs, but also to the structural response of thin films by hydrogen diffusion in fuel cells.

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